

LEATHER

Prehistoric man wore hides and skins which were preserved with juices that were extracted from tree bark. Leather provided footwear, garments, holsters for weapons, shelters, and many other products affording protection, comfort, durability, and esthetic properties in a combination that was not attainable from other materials. Despite efforts, particularly during the last 30 yr, to produce leatherlike materials (qv) from other fibers, sheet materials, and petrochemicals, and to substitute them in the marketplace for leather products, leather still is the product of choice by the consumer. The demand for leather far exceeds the supply, and the principal function of the substitutes has been to fill those needs for which the supply of leather is inadequate.

In the leather industry, supply bears no relationship to the demand for leather and leather goods. The hides and skins that are used for leather manufacture are by-products of the meat industry. As more meat has been consumed by a growing world population, more hides and skins have become available so that more leather is being manufactured than ever before. Yet the growth has been far below the growth of the consumer-goods industries and the demands for footwear, gloves, luggage, handbags, small personal leather goods, and garments. Synthetics have not displaced leather

but have allowed it to be used where it is best suited and most needed. For example, as nonleather soling materials for shoes improve in quality, the shoe-upper leather manufacturer can buy more hides to make more uppers and more shoes can be produced to accommodate more people who have less need for the genuine comfort of an all-leather shoe. Leather-sole production and use stabilized at the point necessary for those people who could not tolerate synthetic soles because of excessive foot perspiration which could not be transmitted by the upper alone or because their feet were too tender to withstand the greater impact felt through synthetic soling materials. Substitutes for leather range from fabric (in garments) to rubber and synthetics (in shoes); rubber and synthetics account for nearly 90% of all shoe soles. Synthetic materials have been only moderately successful in displacing upper leather in shoes. Where comfort and durability are important, leather will continue to be the dominant material used. Similarly, leather upholstery has been replaced partially by synthetics, eg, vinyl-coated fabrics which provide alternative coatings for items such as cushioned chairs, sofas, and bar stools; but this field also has stabilized, and the use of leather again is growing as it meets needs for durability, long term flexibility, low heat conductivity, and resistance to tearing at stitches, none of which properties can be met by the synthetics; no synthetic material has ever duplicated all of the useful properties of leather. Leather has been used as industrial belting, where its properties of maintaining physical form, grease resistance, high strength, and extreme low temperature flexibility have been important.

Thus far, hides have been sold for leather manufacture at prices far exceeding those for any other potential use. If, for any reason, demand for leather should be less than supply, the price of hides could drop to about a hundredth of its present price before it would be used for markets not already saturated by the current trimmings and other losses from hides in process. However, because leather is so highly qualified for a variety of uses, the principal competitors for hides are other leather manufacturers for other end-use fields, and drastic price reductions of the type discussed most probably will not occur. (All aspects of the chemistry and technology of leather are reported in ref. 1.)

Physical Properties

Leather has unique properties which make it ideally suited for use in the manufacture of a variety of products, the most notable being footwear. Extremely large variations exist in leather properties because of differences in the types of skins employed, ranging from the loose open structure of a sheepskin to the hard shell-like area of a horse butt used to make the long-lasting, tough cordovan. Variations in processing induce large changes in physical properties even in the leather from a single animal type, eg, cattle. However, cattlehide leather, which is cut to different thicknesses, given different types of soaking, unhairing, pickling, tanning, lubrication, and finishing, can be manufactured with carefully specified and very different properties for varied uses.

Even if leather is considered for a single use, eg, shoe uppers, a large variation in properties is advisable to allow for different shoe types, eg, casual, military, work, or dress shoes. A range of values for various physical properties of cattlehide shoe upper leather, a representative value, and references from which these data were gathered are listed in Table 1. A general discussion of the factors involved in the tests for leather has been reported (2).

Table 1. Physical Properties of Shoe Upper Leather

Property	Range	Representative value	References
tensile strength, MPa ^a	15.26–37.48	27.6	3–5
elongation at break, %	29.5–73.0	40	3–5
stitch tear strength, N/cm ^b	1280–2275	1751	3, 5–7
tongue tear strength, N/cm ^b	226–961	525	3, 5
thickness, mm	1.5–2.4	1.8	4, 6
bursting strength, kN/cm ^b	1.10–24.5	17.5	3–4, 6
grain-cracking, N/cm ^b	525–1489	1051	3–4, 6
wet shrinkage temperature ^c , °C	96–120	100	6, 8
apparent density, g/cm ³	0.6–0.9	0.75	2, 4
real density, g/cm ³	1.4–1.6	1.5	2, 4
flexibility (Flexometer)			
bending length, cm	6–9	7	4
flexural rigidity, mg/cm	10,000–50,000	20,000	4
bending modulus, MPa ^a	19.7–68.9	34.5	4
compression modulus, MPa ^a		0.345	4
cold resistance ^d , K			
(workable without cracking at			
heat resistance	shrinks depending on moisture content, anhydrous decomposition at 160–165°C	92	9
temper of chrome side leather (butt)			10
flexibility factor, g		400	11
recovery, %		57	11
resilience, %		21	11

^a To convert MPa to psi, multiply by 145.^b To convert N/cm to lbf/ft, divide by 14.6.^c Chrome-tanned leather values.^d Ordinarily limited by finish-crack or lubricant hardening properties.

One of the most important properties of leather and one for which there is a paucity of quantitative data, is the ability of leather to conform to the shape of the foot. Shoe sizes are quite standard, yet there is much variation in the shape of individuals' feet. However, these variously shaped feet fit into standard shoes because the leather gives at points of pressure. Yet, the leather maintains its shape and is not deformed beyond the point necessary to give foot comfort, so that it does not become baggy even though the distended part is subjected to repeated flexure. This may be ascribed to a favorable balance between plastic and elastic flow in leather. Plastic flow imparts the necessary give to provide foot comfort; elastic flow is responsible for the maintenance of shape by ensuring proper recovery during flexing action. Leather substitutes have not achieved this combination of properties.

Materials employed as leather substitutes have been able to function in uses where only protection and flexibility have been the chief requirements, eg, in upholstery, luggage, belts, and shoe soles. However, substitutes have not been able to conform to the shape of or to remove moisture from the foot. The amount of moisture from foot perspiration is considerable, although it varies greatly among individuals. For example, in an 8-h test of five subjects under conditions of moderate exercise at 23.9°C, the amount of perspiration emitted by one foot ranged 15–50 g with an average of 34 g (12).

It was believed that water vapor was transmitted through the free spaces within the leather (13) or by condensation in small pores of the leather on the more humid side and migration of the condensed liquid through capillary action toward the less humid side where it would evaporate (14–15). This belief has persisted even though it has been demonstrated that leather impregnation could drastically lower air permeability without significantly lowering water-vapor permeability (11).

Probably only a part of the transpiration of water through leather results from passage through leather interstices. The mechanism of the transmission of water vapor through leather has been demonstrated to be a function of the material rather than a linear diffusion process (16–17). The evidence indicates that water is sorbed at polar groups of the protein molecules and is conducted by an activated diffusion process along the fibers, even against an air-pressure head. Transmission of water vapor through leather is affected by filling the interstices of the leather with grease or other materials, but the range of air permeability changes ca 200 to 1 as contrasted with a change of ca 2 to 1 for water-vapor permeability. According to the mechanism of water-vapor transmission by active diffusion along polar groups of the internal protein surfaces of the leather, a certain amount of energy would be required to free sorbed or bound water from an active site before it can go on to the next site. This energy is the energy of activation for permeation and was measured at 15.0 kJ/mol (3.58 kcal/mol).

Manufacture

Raw Material. Chemical Composition. Fresh cattlehides, like most biological materials, contain 65–70% water, 30–35% dry substance, and less than 1% ash. The dry substance is largely made up of the fibrous proteins (qv), collagen, keratin, elastin, and reticulin. The main components of the ash, listed in decreasing concentration, are phosphorus, potassium, sodium, arsenic, magnesium, and calcium.

Collagen is the leathermaking protein of the hide. The tanning process consists of a number of collagen-purification steps prior to the actual tanning of the hide. If most of the minor proteins of the hide are not removed before the tanning, they seem to prevent the resulting leather from being soft and flexible. The corium is almost entirely collagen. This protein, which is ubiquitous in the animal kingdom, is unique in its amino acid composition and physical properties. Collagen is responsible for the strength and toughness of the raw hide and of the leather made from it. It is the principal component of connective tissue, and changes in collagen structure have been postulated to be important to aging. A great deal of research has been carried out regarding the structure and function of collagen, and a number of reviews have been published (18–21).

The hair is composed entirely of the protein, keratin, which is the second most common protein in the hide and, depending on the age of the animal and season of the year, may constitute 6–10% of the total protein. One of the first steps in the manufacture of leather is removal of keratin from the hide.

Smaller amounts of other proteins are associated with the hide. Myosin, a muscle protein, is found in the *erector pili* muscle in the grain layer. Various globulins, albumins, and mucoproteins also are present. They probably are residuals from blood as well as interstitial proteins. Elastin is the primary protein, other than collagen, that is present in the grain layer. This connective tissue protein is quite elastic and is re-

sistant to temperature denaturation and proteolytic degradation. Very little elastin is found in the corium.

Lipids are the next most abundant chemicals in hides. The grain layer is ca 9% lipids on a dry weight basis; this fraction includes waxes, phospholipids, sterols, and fatty acids. Most of the lipids are found in the sebaceous glands around the hair follicles. The corium layer is quite variable in its lipid content and may contain from 1–11% lipids. These are, primarily, triglycerides which are randomly distributed in fat cells. Diet and age seem to correlate with the presence of fat cells in the corium.

A small amount of carbohydrates is present in the hide in the grain layer. These compounds largely are mucopolysaccharides which are believed to act as a lubricant for elastin.

Microstructure. The skin forms a tough, protective, thermal blanket on an animal and is vital to the animal's existence; it also provides an ideal raw material for leather. Microscopic examination reveals the physical structure that is responsible for skin's unique properties (Fig. 1). In general, all mammalian skins are composed of a dense, interwoven, fibrous mat in the center (dermis, including grain and corium); a thin, cellular outer layer (epidermis) with protruding hairs; and a loose, fatty, inner (subcutaneous) layer attached to underlying muscles. The looseness of the inner layer facilitates mechanical removal (flaying) of the skin in the slaughterhouse.

The dermis is composed of two layers with distinctly different structures. The upper portion, including the entire length of hair follicles in most species, is called the grain layer by tanners. An exception to this is pig skin, in which the hair follicles extend through the entire thickness of the dermis. The numerous components of the grain layer in cattle hide are illustrated in Figure 2 (enlarged from Fig. 1). Each hair follicle, or pocket, is associated with its surrounding epidermis and with an oil gland, a sweat gland, and an erector muscle. This cellular conglomerate serves protective, sensory, and excretory functions in the living animal as well as controls skin temperature by increasing or decreasing evaporative cooling at the surface. At the junction of epidermis and dermis, there is a coarse basement membrane which, after separation of the epidermis, becomes the grain surface (enamel) of leather. The grain layer also contains a network of small blood vessels and capillaries. Interwoven among these cellular components is a three-dimensional mat of thin collagen fibers which become the leather substance. Interspersed among these fibers, especially in the upper half of the layer, are thinner, elastic tissue fibers that are arranged mostly parallel to the surface. When the cellular structures have been decomposed by chemical processing, the resultant fibrous mat has many voids and reduced density.

The corium is a much simpler structure than the grain layer and is composed mostly of thick bundles of collagen fibers. These bundles are interwoven in a fairly random, three-dimensional pattern, but the angle of weave in a vertical direction tends to vary with animal species and, especially, with location on the body. The excellent strength and stretch properties of leather depend largely on corium fibers and their prevailing orientation. There also are some scattered blood vessels and elastic tissue fibers in the corium layer and variable fat deposits in animals that were intensively fed. In fresh skin, the dermal structures are embedded in a semifluid gel or ground substance. Chemical processing opens fine spaces between fibers but otherwise does not alter the gross physical structure of the corium as it does the grain layer.

At the molecular level, collagen is synthesized in the dermis by elongated cells called fibroblasts and then aggregates into unit fibrils and fibers. Because of their

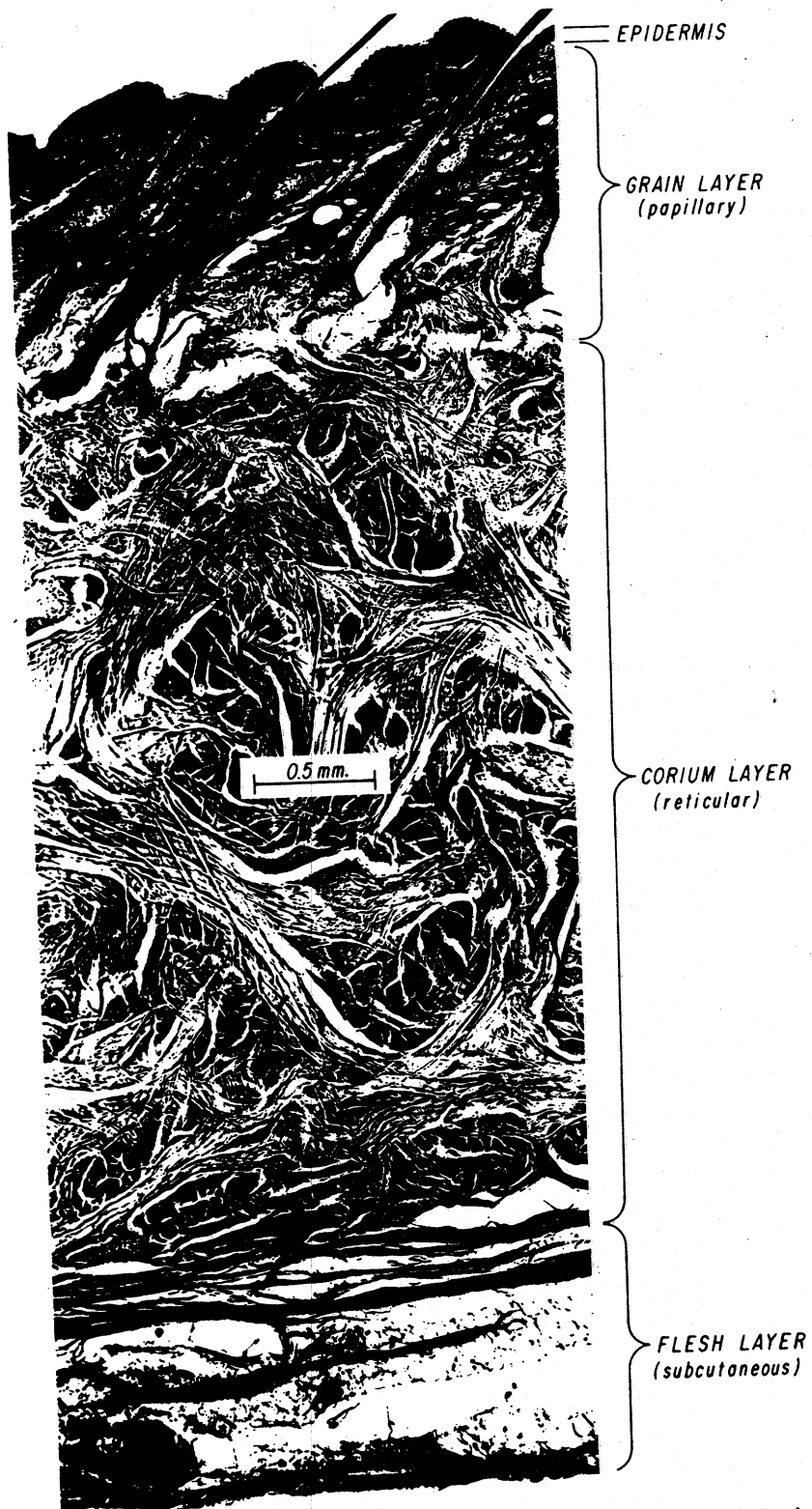


Figure 1. Cross section of cowhide showing subdivision into four principal layers. The dermis, which includes the grain and corium layers, becomes the fibrous substance of leather.

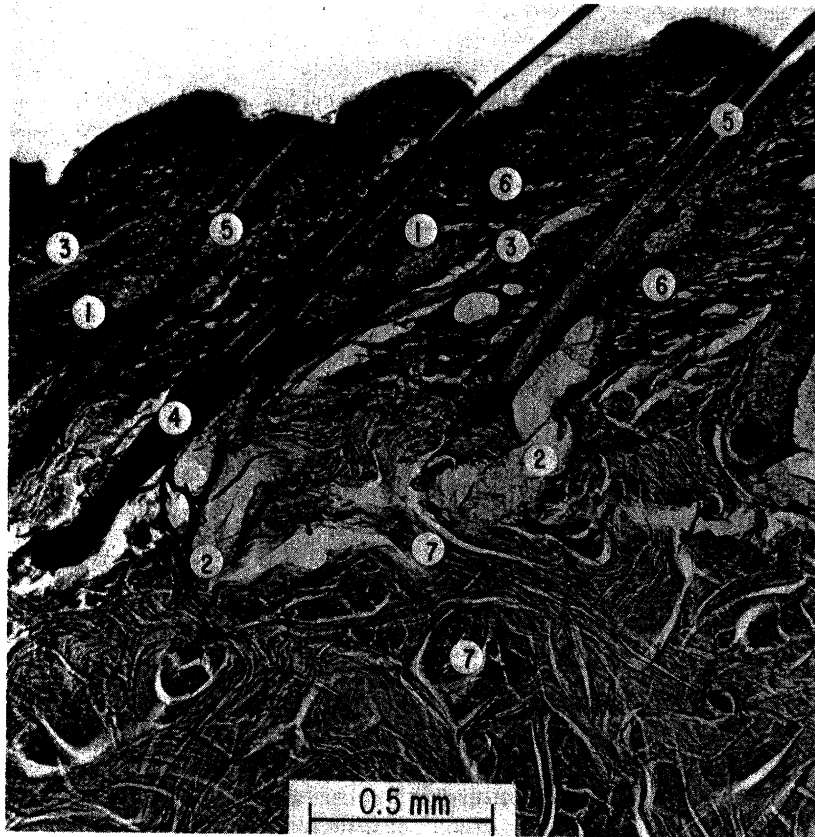


Figure 2. Enlargement of grain layer and upper corium showing components: (1) oil or sebaceous gland; (2) sweat or sudoriferous gland; (3) hair muscle or *erector pili*; (4) growing hair; (5) degenerating hair; (6) fine fibers of elastic tissue; (7) collagen fiber bundles shown in longitudinal and transverse section.

extremely small size, the unit fibrils must be visualized with an electron microscope. Figure 3 (22) shows a thin section of cowhide at high magnification (ca $\times 17,000$). Lengthwise fibrils, with their characteristic cross striations, can be seen in one corner; elsewhere, the fibrils are seen in cross section as they are organized into two small fibers. These fibers are arranged with others in parallel alignment to form larger fibers and, finally, fiber bundles. Ordinary light microscopy may be used to examine the interrelationships of all structures at lower, more practical magnifications.

Although mammalian skins generally are similar in most respects, the species that are used for leather display a number of minor variations which are often important. For example, skins from wool-bearing sheep contain an unusually large number of hair follicles per unit area and a characteristic fatty layer at the base of the follicles which affect processing procedures as well as final properties. Anatomical differences must be known in order to make the best use of each type of material. These differences also add to the esthetic appeal and variety of leather, since modifications of the surface grain pattern are formed by follicle openings. Inspection of full-grain leathers with a hand lens reveals distinctive patterns which, in most cases, can be used

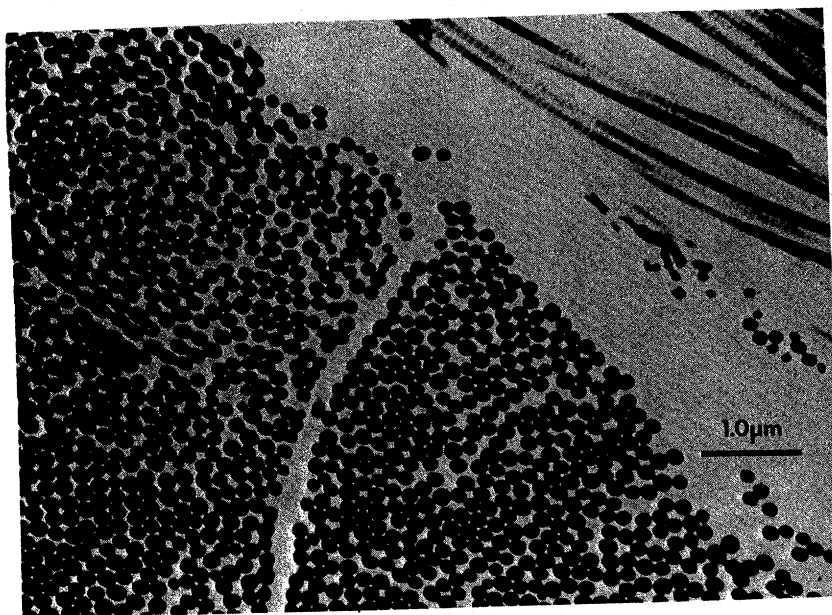


Figure 3. Electron micrograph of hide cross section showing, at upper right, longitudinal collagen fibrils with typical striations and, elsewhere, a cross section of fibrils comprising two small fibers (22).

to fingerprint the species of origin, unless an embossing technique has been used to imitate a different species. This inspection may be augmented by a similar inspection of a freshly cut edge to expose the internal structure and, thus, add to the reliability of identification (11,23-27).

Defects. Significant defects which seriously mar the surface appearance or impair the physical properties of leather can occur anywhere in the manufacturing process, ie, from the living animal to the finished product. Some of these may result from poor flaying technique in the slaughterhouse, inadequate preservation and handling methods, or improper use of chemicals and heat in the tannery. Wherever they occur, defects are costly to some phase of the industry and, ultimately, to the consumer. Although much progress has been made in minimizing this wastage, much remains to be done.

A comprehensive review illustrating the nature and cause of most skin and hide defects has been published (28). Many animals suffer scratches or punctures from barbed-wire fences, prods, or other sharp objects which leave their marks as visible scars on the skin. A more serious type of scar, which is man-made and, thus, preventable, is the brand produced by application of a hot iron for identification purposes. Hot branding is a traditional practice in the U.S. and is responsible for major economic losses. A less damaging system of freeze branding was developed (29) but, for various reasons, it was not found suitable by the beef-cattle industry, although it is commonly used for horses and dairy cattle. A better, nondestructive identification system is needed. Potentially useful ideas include the insertion of an electronic transponder under the skin of the animal to transmit a coded number to a portable interrogator/receiver or the use of a laser device to bleach the hair pigment in a given pattern (see Lasers).

Among the various skin diseases that affect domestic animals, those that are caused by parasites probably affect leather quality the most. For many years the damage from grub or warble holes in cattlehides and associated losses of meat caused by migrating larvae (*Hypoderma* spp.) have been costly to both tanners and meat packers despite the development of preventive treatments. Another problem is the grain damage to cattlehides and goat skins caused by demodectic mange mites (*Demodex* spp.); although this damage (30) is less severe but still significant, more research effort is needed to discover an effective treatment. The cockle defect of sheepskin seriously damages suedes, shearlings, and other types of leather and has been attributed (31) to a parasite, the common sheep ked (*Melophagus ovinus*), and good preventive treatments are known. However, because it does not seriously threaten the life of the animal, the condition is not routinely treated, and it continues to damage leather and reduce the values of meat and wool (qv).

Another parasite problem, which continues despite the availability of good treatment methods, is the damage from many species of ticks (30). Ticks also can transmit serious diseases, but the insects are most prevalent in hot climates and are less important to maintaining hides in the U.S. A number of skin diseases caused by bacteria, fungi, or viruses are most prevalent in warmer climates, and few of them seriously threaten U.S. livestock.

An important biological defect that is most prevalent in a major breed of U.S. beef hides, but has received only limited attention, is the vertical-fiber defect (32) known as pulpy butt. This consists of an inherent, abnormally vertical orientation of the corium fibers which leads to extremely weak leather and many shoe failures. The condition is localized in the choice area of certain hides, is difficult to detect in raw material, and is thought to be hereditary. More research might resolve the remaining genetic uncertainties and, thus, justify a breeding approach to control it.

Animal growers play a more significant role in the production of good leather than they realize. Full use of available technology could improve the quality of the product. Among the defects mentioned, only brands and grubs are obvious enough to be detected in the classification of raw material, and their presence lowers the purchase price. The other defects remain hidden until processing. The economic losses are most apparent in the case of brands. The price differentials between branded and unbranded hides amounted to ca $\$50 \times 10^6/\text{yr}$ (33), and this loss was passed to the cattle growers. Another $\$50 \times 10^6$ was lost by the tanning industry in wasted costs for processing unusable parts of branded hides. The total loss of $\$100 \times 10^6$ has risen because of inflation.

Chrome Tanning. Practice. The primary function for a tanning agent is to stabilize the collagen fibers so that they are no longer biodegradable. Over 95% of all the leather manufactured in the United States is chrome tanned. The manufacture of leather can be divided into three separate phases. Historically, the first took place in the beamhouse where the skin was prepared for tanning. The next phase was done in the tanyard. The last phase is finishing. The beamhouse was so named because the steps carried out in this part of the process originally were carried out by hand, with the skin laid over a log or beam. Tanning was done in an outdoor tanyard in pits or holes in the ground containing the tanning solutions. Finishing was developed much later and protects the grain surface of the hide and enhances its appearance. Although methods have changed greatly, the beamhouse and tanyard still exist in modern tanneries. Discussions of this subject are available (1,27). Some of the proteins in the raw skin

must be removed in order to make satisfactory leather. In addition, the collagen fiber structure must be modified to allow full and uniform penetration of the tanning chemicals. All of the following factors have an effect on the product of any step of the leathermaking process: temperature, time, concentration of reactants, and the amount of mechanical action.

The hides generally are received by the tanner in a salt- or brine-cured condition. The curing dehydrates the hide, which may contain as much as 14% of its weight as salt. A fresh hide contains ca 64% water; after brine curing it contains ca 45% water and 41% protein, only $\frac{2}{3}$ of which is leathermaking collagen. The first step taken by the tanner is to remove the salt and to rehydrate the fibers by soaking. A detergent usually is added to speed up the hydration. The soaking procedure also removes water-soluble proteins and washes the hide free of manure and dirt. The period of soaking generally is from 12–24 h.

Next, the hair must be removed. The keratin has a large content of sulfur-containing amino acids, mainly cystine (see Amino acids). This amino acid's disulfide cross-links stabilize the protein molecules, resulting in a stable hair fiber. Hair removal can be accomplished with a saturated solution of calcium hydroxide (lime) alone or in combination with a sharpening agent, eg, arsenic or cyanide (both of which are no longer used) or sodium sulfide or sodium sulfhydrate. Lime by itself does not dissolve the hair but only loosens it in the base of the hair follicle for easy removal by an unhairing machine. This labor-intensive apparatus scrapes the loosened hair from the surface of the skin and is termed a hair-save process. Lime (qv), by itself, requires from 5–7 d to loosen the hair.

Because of the small market for hair and the importance of time, a hair-burn process more commonly is used. Although sulfide at a pH greater than 11.5 can dissolve the hair in as little as 30–40 min, the usual sulfide unhairing process takes from 4–6 h. Although it is rapid and requires less manpower than the hair-save process, it contributes heavily to the pollution load (BOD) in the tannery effluent.

In many tanneries, the relatively brief unhairing step is followed by a longer (4–16 h) liming step. The spent unhairing liquors with the dissolved hair are drained from the hides and a fresh saturated lime solution is added. The action of lime not only loosens the hair but opens up the collagen fiber structure. Collagen swells outside of its isoelectric point in either acid or base in 8–48 h. This swelling leads to subsequent fiber separation and allows rapid penetration of tanning chemicals. Additional proteins also are removed in the liming stage, and some hydrolysis of amide side chains of the collagen to acid side chains takes place and aids the tanning reaction, since the acid groups are the primary source of binding for chromium tanning agents.

The liming step, when complete, is followed by deliming and bating. The hide is washed to remove soluble lime and hair particles. At this point, the stock is at a pH of 12.5. The most widely used deliming salt is ammonium sulfate, which lowers the pH to 8–9, a range in which the enzymes in the bate can act properly. The bate is a preparation of pancreatic enzymes that usually are absorbed on sawdust. The effective enzymes are proteases which break down additional miscellaneous proteins (see Enzymes, industrial). Bating action usually is short, ie, ca 1–4 h. Immediately after the bating, the hides are pickled with sulfuric acid to lower the hide pH to less than 3. Sodium chloride is added to prevent acid swelling. A full pickle requires at least two hours. Because the addition of a strong acid to water generates a great deal of heat, care must be taken to prevent denaturation of the collagen. Once the hide is in the acid condition, it is prepared for the tanning operation.

At a pH of 2.8, chrome sulfate (usually ca 33% basicity) is soluble. After the tanning solution has been allowed to fully penetrate the hide, the pH is raised slowly with sodium bicarbonate. By the time a pH of 3.4–3.6 is obtained, the chrome has reacted with the collagen to produce a fully preserved, tanned hide. At this point, the hide is said to be in the blue. Although specific procedures are followed in the beam house for a particular type of finished leather, the blue stage allows many options in the next phases of leather manufacture.

The tanned hides generally are stacked overnight and the chrome further fixes onto the collagen. They then are put through a hide wringer so that they are almost dry to the touch and then are sorted for quality and thickness. Each hide is selected to be made into a particular leather product line, eg, to be heavy- or lightweight shoe leather, to be naked grain, or, because of poor grain condition, to be heavily finished. Once the choice has been made, the hide is split to the desired thickness. The split, which is from the flesh side of the hide, is either sold to a split tanner or is processed further in the same tannery to make split leather.

Theory. Chrome tanning generally is carried out by adding the acidified hide to an aqueous solution of trivalent chromium sulfate of 30–50% basicity. By using a combination of gel-permeation chromatography, gel electrophoresis, ion-exchange chromatography, and spectroscopic techniques, it was established that there are at least 10 ionic and neutral complexes in a 33% basic chrome sulfate solution (34) (see Chromium compounds). The structures of eight of these were determined along with the relative amounts of each. The six compounds present in highest concentration are shown in Figure 4. The simplest ion, Cr^{3+} , with six coordinated water molecules, was present as 9% of the total chrome. The routes of formation of the other complexes resulting from replacement of water with sulfate ion (left side of the figure) or by hydroxide ion (right side of the figure) are indicated. The salient features of the route

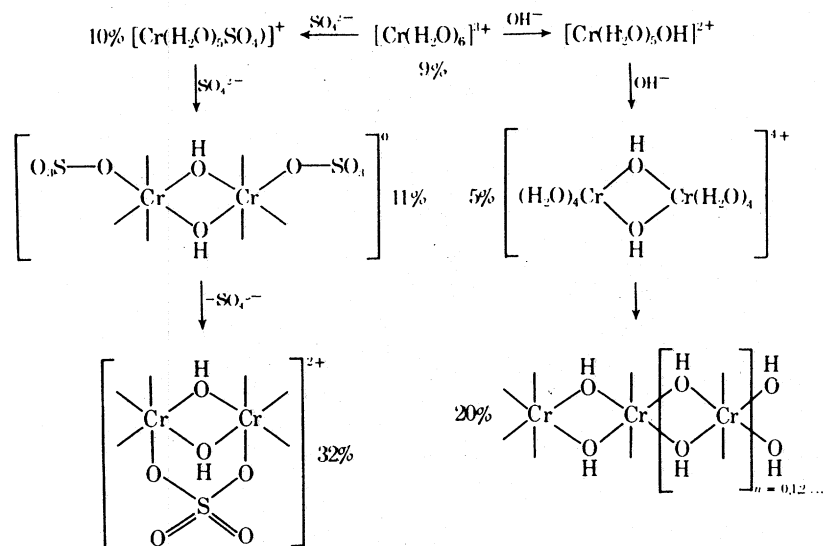


Figure 4. Composition of typical chromium sulfate tanning solution; 33% basic, 0.4 M in Cr^{3+} (34).

of formation of the most abundant species, ie, the 2+-charged, binuclear complex with a bidentate sulfate bridge at the lower left of Figure 4, are the replacement of H₂O by SO₄²⁻ in [Cr(H₂O)₆]³⁺ to give the 1+ monosulfate ion, the formation of the third complex in a series of steps in which OH⁻ replaces H₂O in a pair of ions, and condensation to form the olate-bridged binuclear structure with monodentate sulfate groups. One sulfate group then rotates into the plane of the other, displacing it from the coordination complex to form the bidentate sulfate bridge. This purely descriptive and oversimplified mechanism gives an idea of the type of reaction possible, consistent with experimental evidence and the thermodynamics and stereochemistry of chrome complexes as recently reviewed (35).

The reactions of these basic chromium sulfate tanning solutions with hide collagen have been studied (36). It is firmly established that cross-linking is accomplished by bonding of the various chromium species shown in Figure 4 with free carboxyl groups in the collagen side chains. The liming of hides is effective in providing additional carboxyl groups by chemical hydrolysis of amide side chains.

The reactions that can take place as the carboxylate ions, which are attached to the collagen, enter one of these complexes are shown in Figure 5. The carboxylate group can displace water from the [Cr(H₂O)₆]³⁺ ion (9% abundance) to form monodentate bonds, as shown in the upper equation, or bidentate coordinate bonds with binuclear complexes, as the one shown in the lower equation.

Two mechanisms by which cross-linking can occur (Fig. 6) are straightforward entry of two carboxylate ions into the same chrome complex and olation which involves elimination of water and formation of a linkage between two complexes. The olation reaction is favored by an increase in the alkalinity of the reaction mixture. As the reactions proceed and multinuclear complexes form with multiple olate bridges, hydronium ions are released and highly stable oxalate bridges are formed, as is shown on the right side of Figure 6. There is evidence that bidentate sulfate groups remain in the final complex after curing and drying. Apparently they play a role in improving stability of the complexes.

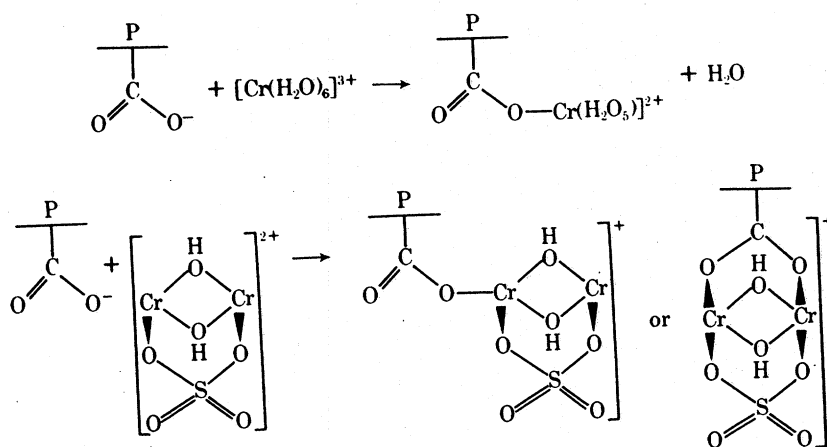


Figure 5. Complex formation with protein (P) carboxyl groups.

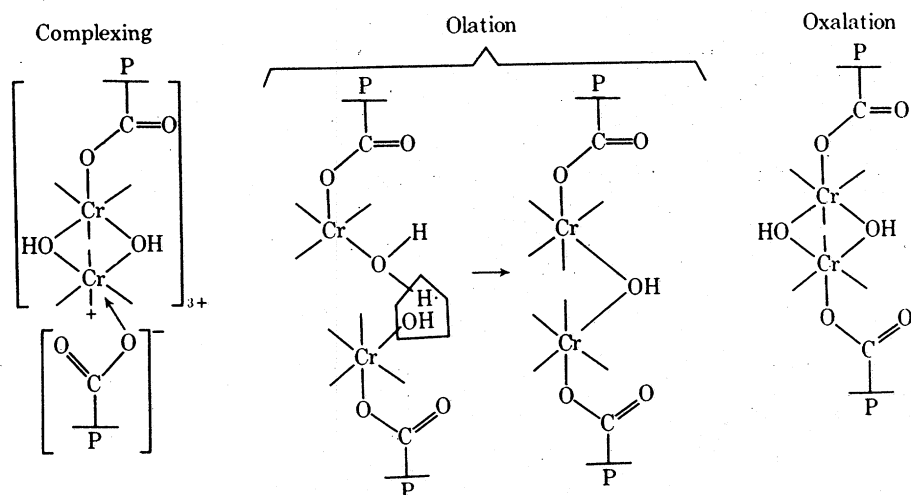


Figure 6. Cross-link formation from chromium complexes (P = protein).

Similar coordination complexes are involved in other mineral tannages. All of these complexes can be reversed or modified by acids, salts, strong bases, and chelating agents. Chromium complexes, although more difficult to form, have the advantage over other complexing cations of reacting much more slowly in these ligand replacement reactions and, therefore, producing leather that is more stable and serviceable in use. Chromium 3+ also is unique in its resistance to oxidation.

Vegetable Tanning. Practice. Vegetable tanning has decreased considerably in importance in the United States; there are only five tanneries producing vegetable-tanned leathers. Leathers made with a full vegetable tannage are used for shoe soles, belts, saddles, upholstery, lining, and luggage. Vegetable tanning produces a fullness and resiliency characteristic of only this type of tannage. It has certain molding characteristics so that, in sole leather, a shoe is produced that adapts to the shape of the individual foot. Vegetable-tanned leathers also have good strength and dimensional stability and, thus, find use in power-transmission belts. Their hydrophilic character is a great aid in shoe linings for the removal of perspiration from the foot.

Vegetable tannins are the water-soluble extracts of various parts of plant materials, including the wood, bark, leaves, fruits, pods, and roots. Some sources contain up to 20% tannin. The extraction process yields a mixture of tannins and nontannins; the higher the proportion of tannins to nontannins, the more valuable the extract. The tannin content is analyzed by an empirical method involving the reaction of the extract with a specially prepared hide powder under specified conditions. In general, the same steps are carried out in preparing the hide for vegetable tannage as are carried out in preparing the hide for chrome tannage, eg, the hair is removed by the same chemicals. However, a much slower process is used and, frequently, involves as long as five days of soaking in pits. The hides are exposed first to saturated solutions of lime and then are moved into other pits in which small amounts of sodium sulfide are present. Initial exposure of the hair keratin to the alkali in the absence of sulfide produces a reaction known as immunization. The main chemical reaction occurring in this process is a

conversion of the cystinyl residues in the keratin to lanthionyl residues; the latter provides a much more stable cross-link to the protein than the former. The resulting hair fiber is much more resistant to chemical attack than is the nonimmunized fiber. At the end of the five days, the epidermis and hair have been loosened in the follicles by the chemicals and are mechanically scraped from the hide in unhairing machines. This lengthy liming and dehairing step is necessary to open up the fibers of the hide in such a way as to prepare them for penetration by the vegetable tannins.

The hides then are mechanically fleshed and returned to vats where they are chemically delimed with ammonium sulfate and bated with pancreatic enzymes. The pH is adjusted ultimately to ca 5. The hides then are placed on frames which are lowered into vats containing tannin solutions and are gently agitated. They are subjected over a number of days to a series of vegetable tannins of increasing strengths. Slow, thorough penetration of the hide is accomplished without case hardening (surface accumulation of tannins). This may be done by moving the frame from pit to pit where tanning solutions of increasing strengths are present or by pumping solutions of tannins from pit to pit over a period of time while the hides remain in one pit. The entire process takes ca three weeks. The tanning liquors normally contain phenolic syntans (synthetic tannins) for color control and naphthalene syntans for sludge dispersancy.

Recently, a more rapid, minimum-effluent vegetable tanning system, known as the Liritan process (37), has been developed. The limed and bated hides are treated for 24 h in a pit with 5% sodium hexametaphosphate (Calgon) solution and sufficient sulfuric acid to achieve a pH of 2.8 at the end of that time. This part of the process has become known as the Calgon pickle. The solution is reused daily, being regenerated with additional Calgon and sulfuric acid, and is discarded only once a year. The treatment presumably prepares the hides for a more rapid vegetable tanning process, and the recommended one with varied concentrations of wattle (mimosa) takes 11 d. Again, the tannin liquors are recirculated and reused. Further finishing of leathers that have been prepared by the Liritan process is the same as for those prepared by conventional processes. First introduced in 1960, the Liritan process has spread throughout the world and is used by the major vegetable-leather tanners in the U.S.

The tanned hides are further processed in order to clean the surface of the hides of excessive amounts of tannins (usually unbound tannin) and then are wrung free of excess water and are oiled. Oiling is carried out in a drum with oils added to lubricate the leather fibers plus a variety of materials that may be drummed into the leather for the purpose of achieving specific properties in the final product. The recipes that are used are largely the inventions of the individual tanner and may include powdered lignin preparations, naphthalene syntan, Epsom salt, corn sugar, salts of organic acids, bicarbonates, and borax. Most of the solids are added as such, the sugar is usually added in the molten form, and the oil, of course, as the liquid. The leather then is hung so as to dry slowly for one week. At the start, air at ca 90–95% rh and no more than 37.8°C is slowly circulated through the drying loft. The relative humidity is decreased slowly so that, at the end of the week, the moisture content of the leather is ca 10–12%.

The grain surface then is sponged with a dilute oil preparation and is rolled repeatedly under considerable pressure with a highly polished metal (usually brass) cylinder on a large pendulum-type machine. The leather is moved back and forth under

the pendulum arm by an operator as the arm strikes down on the leather. The pressure also is regulated by the operator. This operation packs the fibers of the leather and imparts a characteristic gloss to the grain. The leather is allowed to dry, is dip-washed in a solution containing a small amount of wax, is redried, and is given a final dry rolling.

Theory. Functionally, the vegetable tannins are polyphenolic compounds. They are empirically divided into two groups: the hydrolyzable tannins and the condensed tannins. The hydrolyzable tannins are derivatives of pyrogallol. The distinguishing characteristic is that, as a group, they produce solutions when boiled in dilute mineral acids. Chestnut and myrobalan are typical hydrolyzable tannins. The condensed tannins are derivatives of catechol and commonly undergo condensation reactions when heated with mineral acids, thereby producing precipitates (see Hydroquinone, resorcinol, and catechol). Hemlock and wattle are of this type.

It is highly likely that no cross-linking of the protein, other than by the formation of hydrogen bonds, takes place as a result of vegetable tanning. This results from a displacement of hydrogen-bonded water molecules by the phenolic groups of the tannins with the formation of hydrogen bonding between these groups and the peptide bonds of the protein chains. The large size of these molecules and the large amounts of tannin that are used produce a coating on the fibers as well as fill the voids of the leather. In some cases, as much as 50 wt % of tannin is incorporated into the hide.

Sole leather is the predominant leather manufactured by vegetable tanning. Processes for other types of leathers (belts, harnesses) made by vegetable tanning are very similar. Cattlehides are the raw material used for this purpose, with cowhides producing the lighter (thinner) leathers, and steerhides the heavier (thicker) leathers. Historically, sole-leather weight (thickness) has been measured in irons (one iron = 0.53 mm). Cowhides yield leathers ranging from six to nine irons and are used primarily for lightweight shoes, eg, women's shoes; steerhides yield leathers ranging from nine to twelve irons and are used in heavier shoes, eg, men's shoes.

Sole-leather tanning begins with the whole cattlehide; however, parts are removed at different phases of the process and, ultimately, only ca 50% of the hide is sold as sole leather. This 50% is referred to as a double bend or as two bends resulting from cutting the double bend in two down the backbone (see Fig. 7). The bellies, which are ca 25% of the hide, are removed from the pickled hide and are sold for conversion into lining or work-glove leather. The shoulders, which comprise ca 20% of the hide, are removed after tanning and are used for welting leather.

Other Tannages. Chrome and vegetable tannages have greater commercial importance than those that are considered below. Most of these tannages are pretannages or post-tannages for chrome or vegetable processes and are employed to give such qualities as filling, lighter shade for dyeing, and reduction of tannery effluent. Only occasionally are they used alone.

Mineral Tannages. The principal mineral tannage other than chromium is zirconium tannage, and it has been extensively reviewed (38). Zirconium tannage has been compared to chrome tannage but seems to form complexes faster. Stronger-acidity pickles usually are employed to slow the reaction, and the pH is raised more slowly. Extra salt is used to repress swelling at the lower pH. Pretannage with aldehyde sometimes is employed. Zirconium tannage leads to fairly firm, full white leathers, which unlike chrome, are white throughout the cross section. The mechanism of zirconium tannage is unresolved but there seems to be an initial uptake of anionic zir-

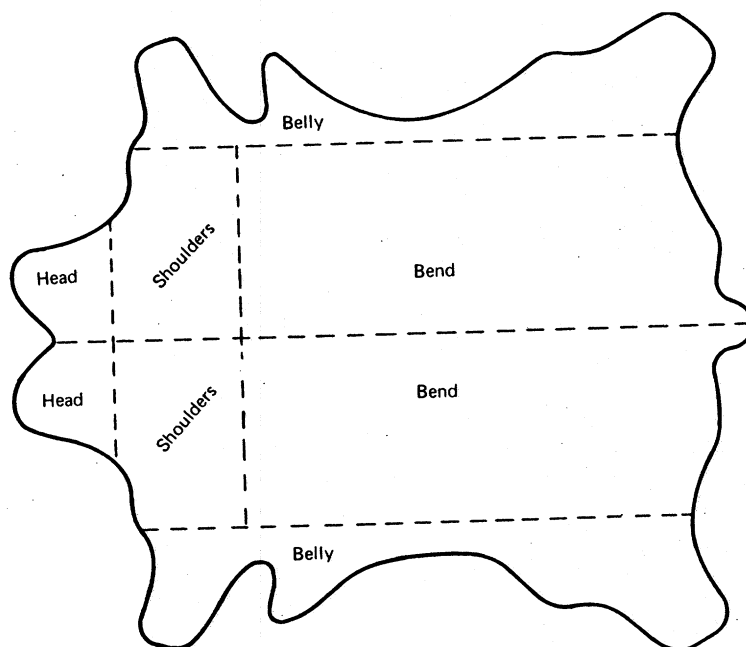


Figure 7. Segmentation of hides for vegetable-tanned leather manufacture.

conium salts at low pH (41). However, for satisfactory leather quality, it is necessary to have subsequent neutralization, which converts the zirconium complex to a cationic state at which time some polymerization may occur.

Aluminum tannage requires very low initial pH and large quantities of neutral salt to repress both swelling and rapid flocculation of aluminum salts as the pH is raised. This type of tannage leads to leathers that tend to dry out and to become hard and horny unless much salt is used; even then, the leather tends to be flat and papery in feel. Aluminum tannage is used in combination with other tannages. Renewed interest in such combination tannages is being generated in view of increasing regulation against chrome tannery wastes. The following recommendations have been made: a mimosa vegetable pretannage followed by aluminum tannage (39), a combined tannage with chromium, alum, and glutaraldehyde with inclusion of acrylic acid polymers to increase aluminum fixation (40-41), and a combination chromium and aluminum tannage to reduce chrome waste (42).

Iron tannage also tends to give flat, papery leather. Initial work indicated poor resistance to aging (43). However, it seems probable that the early leathers received insufficient tannage (44) and two reports indicate better aging resistance than originally was supposed (45-46). Iron-tanned leathers have very little commercial importance, possibly in part because of the intense black coloration produced by iron reaction with phenolics, which are the principal components of the vegetable tannis and syntans so widely employed as retans in tanneries.

Polyphosphates are excellent pretannages for vegetable tanning (47-50). Optimum molecular weights of the polyphosphates are from 1500-2500 (51-53). The Liritan polyphosphate-vegetable combination tannage process (37), as a no-effluent rapid

tannage for sole leather (see Vegetable Tanning), is used by sole-leather tanneries throughout the world.

Silica tannage is effected by the formation of silicic acid and its penetration into the skin in the form of sols of monomeric silicic acid or its low molecular weight polymers. However, for tannage to occur, polymerization of the sols must take place within the skin (44). The silicic acid is fixed to the protein by coordinate bonds and, at the same time, is polymerized in long chains. Difficulties in effecting this reaction reproducibly and leather weakness have hindered the use of silica tannage, although it has been used in some instances to obtain fuller leather in combination with more stable tannages.

Polyphenolic Syntans. Polyphenolic syntans (54–55) are low molecular weight condensation polymers of aromatic phenols, usually with formaldehyde (see Phenolic resins). They usually are sulfonated for increased water solubility. Initially, work on these materials was carried out in order to find a replacement for the natural vegetable tannins that would be consistent in action and easily purified. The variety, availability, and cheapness of the natural tannins, in general, have precluded this approach, except for syntans that were developed as strategic materials when supplies might be cut off in time of war. During World War II, Orotan was developed by the Rohm and Haas Company; it was claimed that Orotan could completely substitute the natural vegetable tannins as the tanning material in vegetable-tanned leathers (56). However, during peacetime and because of their greater cost, the syntans are used extensively only in combination tannages, usually following chrome tannage. They are used to control leather fullness, area yield, color, and the electrical charge of the leather. The latter affects dyeing and fatliquoring operations.

Resin Tannages. The principal resin tannages are those performed with the aminoplast resins. These are low molecular weight, polyfunctional, organic compounds whose reactive groups are *N*-methylol or *N*-alkoxymethyl groups. They usually are made from polyamines, eg, melamine or urea or dicyandiamide, by reaction with formaldehyde and water to form *N*-methylol groups or by reaction with formaldehyde and an alcohol to form *N*-alkoxymethyl groups (see Amino resins). A simple monomeric member of the group is hexa(methoxymethyl)melamine. Alkoxylation need not be carried so far as with hexamethoxymethylmelamine. Residual amino groups can be left. Monosubstitution rather than disubstitution also can be done. The materials are capable of self-condensation to release alcohol, or water for *N*-methylol types, or formaldehyde and they react strongly with amines or alcohols.

The materials used for tanning usually are of low molecular weight, the degree of polymerization being from 2–3, and are water soluble. The reactivity of the *N*-methylol types is greater than that of the *N*-alkoxymethyl types, but the latter are more stable to handling. The low molecular weight materials are incorporated into the leather by drumming. Then the pH is dropped and, under acid catalysis, both self-condensation and reaction with amino and hydroxyl groups of the protein can occur. A review of some tanning procedures has been given (57) and includes discussion of tannage with styrene–maleic anhydride copolymer, tannage with isocyanates, and tannage with furfuryl alcohol, which is condensed *in situ* within the hides by acid catalysis. As yet, none of these is of significant commercial importance.

Acrylic resin syntans containing multiple carboxylic acid groups have gained increased commercial attention (58–59). Such polycarboxylic acid polymers can be expected to increase fixation of mineral tannages (40–41) and can eliminate the possible

toxic hazards from unreacted phenols or formaldehyde which might be present in some of the other types of syntans.

Oil Tannage. Oil tanning produces leathers with unique characteristics (60). Oil-tanned chamois leather is very soft and stretchy, absorbent of water which can be readily squeezed out again and, because it also absorbs grease, is an ideal material for cleaning such items as auto windows and spectacles. The grease is removed from the chamois by alkaline washes with soaps, and the chamois can be reused many times. Because of the softness and suppleness imparted by oil tannage, it also has been used for tanning furs. Here, however, to avoid excessive stretchiness, it usually is employed as a combination tannage with alum, chrome alum, and/or aldehyde tannage.

Chamois leather originally was made from the skin of the chamois, a goatlike antelope found in the French Pyrenées. Now, however, it is made principally from sheepskins with the grain layer split off, although other loose-textured skins are employed. The tanning process consists of stuffing the beamed skins with as much oil as possible (principally unsaturated marine oils) and then subjecting the oiled skins to conditions favoring autoxidation of the oils. Theories of tannage involve not only polymerization of the oil but projections of tannage with aldehydes formed from oxidative chain scission of the oil, epoxy formation, and acrolein formation. However, in view of the necessity for free-radical formation prior to the above processes, the ease of formation of these free radicals on the methylene group alpha to two unsaturated double bonds, and subsequent formation of peroxide free radicals from these (61), it seems reasonable to believe that direct free-radical attack on the collagen occurs. This would form strong covalent bonds that are able to withstand caustic washing. This concept should certainly be a part of consideration of the mechanism of oil tannage. It is analogous to the concept of graft polymerization, a process much studied for leather modification in recent years, both in the United States (62-77) and abroad (78-81). Detailed studies of the autoxidation of oils (82) would seem to give credence to a strong possibility of oil tannage being a form of graft polymerization when such reactions are carried on in the presence of collagenous hide tissue.

Sulfonyl Chloride Tannage. Sulfonyl chloride tannage for chamois-type leather was developed in Germany in World War II with oils from a coal-gas liquefaction process. The fraction that was used boiled from 220-320°C, and it was hydrogenated and then sulfochlorinated to yield a mixture of aliphatic sulfonyl and disulfonyl chlorides, which was termed Immergan. A pretannage with formaldehyde was advised for using these sulfonyl chlorides to make chamois-type leather (60,83-85). However, some researchers (86) found that pretannage with formaldehyde, though helpful, was not necessary. In addition, they noted that the leathers that were produced had excellent cold-temperature properties which were highly beneficial for arctic or other cold-weather usage.

Aldehyde Tannage. Only two aldehydes have commercial use as tanning agents: formaldehyde and glutaraldehyde. With one exception, they are never used as the only tannage but most commonly are used in conjunction with some other tanning agent, usually chromium. The one exception is in the tanning of light-colored, including white, glove leathers (27,87) (see Uses). The functional group in proteins that reacts with aldehydes to form cross-links is the primary amino group of protein side chains of lysinyl residues. Details about the reactions which take place between the aldehydes and the protein amino groups are not known. However, some of the potential reactions

which should be considered are shown in Figure 8 (88). Formation of a methylol or substituted methylol derivative certainly is the first step; however, following this formation, several alternatives are possible. Direct substitution of an amino group for the hydroxyl is one. This leads directly to a hydrolyzable cross-link in a protein. Addition of more aldehyde can take place and, for those aldehydes having hydrogens on the α carbon, Schiff's base formation also can take place. In the latter case, further steps in the reaction sequence can lead to condensation reactions of the type shown. These have been proposed for glutaraldehyde cross-linking. Glutaraldehyde is a difunctional reagent and both ends of the 5-carbon chain can take part in these reactions.

One important difference between the tannages achieved with these two aldehydes is that formaldehyde forms cross-links that are disrupted easily by simple hydrolysis, whereas glutaraldehyde forms cross-links that are completely stable even to hydrolysis with strong acid. Thus, there is a considerable difference in the relative stabilities of the two tannages. Another difference is that formaldehyde tannage yields a white leather, whereas glutaraldehyde tannage produces a light-tan leather. When these aldehydes are used with other tanning agents, the color imparted by the additional tanning agent changes the results. One combination that has been used successfully to produce a white leather is that of formaldehyde and aluminum.

The principal raw materials for the production of high quality, light-colored glove leathers are kid skins and hair sheepskins. These skins are processed with conventional chemicals through soaking and unhairing, fleshing and degreasing, and pickling. They then are tanned with from 6–12% formalin, based on the weight of the pickled skins. The starting pH for this tannage usually is ca 2 or 3 in ambient temperature conditions. During the tanning reaction, which usually takes ca 16–18 h, the pH gradually is raised and the temperature is increased. The final temperature of ca 35°C and a pH of ca 7 is common. Further processing includes the use of retannages and fatliquors to maintain the white or light color of the leather. For darker-colored glove leathers, a combination of chromium and formaldehyde tanning commonly is used. Aluminum sometimes is used to increase the stability of the white or lighter-colored leathers, and this combination also is frequently used for fur tannages.

The retannage of vegetable-tanned leather with formaldehyde, which reacts under

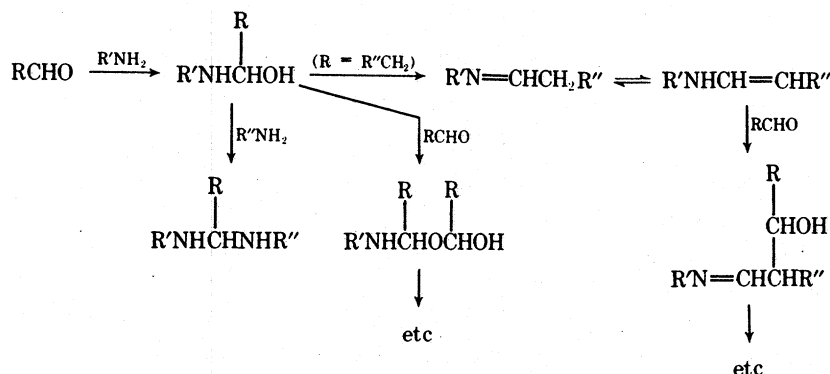


Figure 8. Aldehyde-amine reactions.

acidic conditions and increased temperatures with the polyphenolic vegetable tannins, provides a more stable tannage. Formaldehyde retannage of vegetable-tanned insole leather increases the resistance of the leather to perspiration.

Glutaraldehyde is most frequently used as a retannage for chrome-tanned leather. Glutaraldehyde tanning results in the formation of extremely stable cross-links in the protein. Although numerous investigations of the nature of these cross-links have been made, their identity is unknown. The stability of this tannage to hydrolytic conditions has led to its use in the production of leathers with improved resistance to hot soap solutions, to perspiration, and to alkalis. Thus, leather for use in gloves, garments, work shoes, and nurses' shoes frequently is made by retanning chrome-tanned leather with glutaraldehyde. Other improvements resulting from the use of glutaraldehyde retanning include a more level coloring and a better mellowness of the leather.

Although the most frequent use of glutaraldehyde is as a retanning agent, following chrome tanning, it can be used quite effectively with vegetable tanning either as a pretanning agent or as a retanning agent. When used in the former manner, the subsequent penetration of the vegetable tannin extract is very rapid and the properties (eg, shrinkage temperature, water solubles, and perspiration resistance) are much improved. When used in the latter manner, it leads to improvements in these properties in addition to an increase in thickness of the leather.

Post-Tanning. Retanning, Dyeing, and Fatliquoring. During the early aging period, when the leather is stacked, there is a gradual decline in the pH of the stock as increased chrome fixation, ololation, and oxolation occur. Consequently, after transfer to a drum, the stock is neutralized to a desired pH, frequently is retanned, and then is dyed and fatliquored in rapid succession in the same drum.

The acidic, chrome-tanned leather is highly cationic in nature, since it is well below the isoelectric point of collagen which, after the liming process, has an isoelectric point of 5.4. Neutralization pushes leather closer to the isoelectric point and reduces the surface charge on the protein. This is important because many of the dyes that are employed are anionic. If the leather is too cationic, the precipitation of the anionic dye at the surface occurs rapidly, the dye is confined too much to superficial layers, and the dye is considered too astringent. Neutralization of the surface layer slows the cationic/anionic interaction and allows deeper penetration of the dyestuff. Retannage also affects the surface charge on the leather. Many of the syntans employed for retannage are salts of naphthalene sulfonates or other organic sulfonates having an anionic charge. They occupy many of the cationic sites on the leather and, thus, change the net charge and affect dye penetration and combination. The natural vegetable tannins and polyphenolic syntans also are anionic in character and affect the dyeing process. If highly vegetable-retanned, the leather composite becomes anionic and usually requires the utilization of basic dyes. Hence, vegetable retans are used not only to impart vegetable-tanned leather characteristics, eg, the dimensional stability to changes in relative humidity, increased fullness and temper, and ability to be tooled, but for their effects on leather dyeing and appearance.

Fatliquoring is the application of oil-in-water emulsions to the leather. It usually succeeds the dyeing process, although some tanneries apply them simultaneously rather than in rapid succession. The oil emulsions usually are drummed in at elevated temperatures. Commercially used oils usually are of animal or vegetable origin and of relatively low iodine number, although cod and other marine oils are sometimes included but usually in minor amounts. Fatliquoring emulsions may be anionic,

nonionic, or cationic. Blends of nonionic with one of the other classes frequently are employed to assist oil penetration; the nonionic surfactant prolongs the stability of the oil after its anionic or cationic charge has been neutralized. Protective colloids, eg, gums, starches, and proteins, also can be used to prolong emulsion stability, and emulsions prepared in their presence frequently are of finer particle size than otherwise is obtained. Anionic fatliquors usually are prepared from mixtures of either sulfated or sulfonated oils with raw oils. Cationic fatliquors usually are blends of alkylated long-chain amines together with raw oils. However, synthetic surfactants of the desired type may be added to both. The polar components tend to be bound to the protein, probably mostly by ion-dipole interaction. The raw oils have more freedom to migrate but tend to stay in the area of the bound oil, probably by a process of mutual solubility. The principal function of the fatliquoring oils is to reduce the amount of fiber cohesion during the drying process. Lubrication of the leather is an important but secondary effect. Because oil distribution is much affected by the distribution of ionic charges in various strata of the dyed and undyed leathers, a variety of tempers, flexibilities, and stretch characteristics can be attained. Dyeing and fatliquoring are reviewed in detail in refs. 89-92.

Drying. Once all of the wet operations have been completed, the leather can be dried which not only involves removal of excess water, bringing the moisture content close to that of the finished leather, but completes the reactions of some of the materials (eg, tanning agents, fatliquors, and dyes) with which the hide has been treated (see Drying) (27,93-94). Leather drying occurs by removal of water first from the surface of the leather and then by a diffusion-controlled process from within the leather. If drying at the surface occurs too rapidly before the diffusion can occur, the surface becomes dehydrated and, eventually, hard and the interior remains moist. If dehydration proceeds too far, the surface can never be rewetted completely. Thus, the drying operation must be carefully controlled. Properly tanned leather can be dried more rapidly and easily than untanned collagen. One of the criteria of a tannage is that the leather is soft when dry. The extent to which this is the case depends on the type of tannage and other materials (fatliquors especially) present. Even so, drying is accomplished under carefully controlled conditions of temperature, humidity, and air circulation.

The most fundamental and oldest method involves simple air drying of hides and skins that are hung over supports. Currently this is done, but the drying chambers are programmed in some manner to control the conditions. Since the hides and skins are not held in any shape, ie, restrained, shrinkage occurs with a resulting area loss. To a limited extent, this problem has been overcome by tacking the hides and skins flat to boards. A variation of the above is toggling. In this practice, the hides and skins are stretched out over screens or perforated plates, called toggle frames, and are clamped in place. The frames that contain the wet hides and skins are placed in drying units. Large units are available with several frames mounted on tracks so that the frames can be easily slid into and out of the units.

Another method involves pasting the hides or skins, grain-side down, to plates of glass, porcelain, or metal. These plates are mounted on tracks that move into and out of large drying units. The leather dries from the flesh side only and a smoother, flatter grain is achieved on the leather.

The most recently developed method is vacuum drying. The hides and skins are spread out, grain down, on a smooth, highly polished, heated, stainless steel plate in

which the temperature is carefully controlled. A cover is lowered and sealed over the plate and the space between is evacuated. This method permits rapid drying with few problems with the product quality because the conditions can be controlled much more accurately than by other methods.

Coatings. In the process of making leather from hides or skins, great pains are taken to make a uniform product. A manufacturer of a particular type of leather will use a particular animal species. Yet because of variations in individual animals and their nutritional and environmental histories even within that species, manufacture starts with a very variable substrate. The skins vary in thickness, in the angle of weave (95) of the fibers, and in natural defects, not only from animal to animal, but from area to area of the skin from the same animal. The leather manufacturer minimizes these differences by using processes as uniformly as possible, by splitting and shaving the leathers to uniform thicknesses, by tanning and filling to occupy the voids in the looser-structured flanks, and by using mordants to obtain as level dyeing as possible. However, it is the finishing process with its application of natural or synthetic polymers and of colorants, within and on the surface of the leather, which produces the uniformity, appearance characteristics, and resistance to scuffing and abrasion which are required for a commercial product.

Coatings (qv) for leather function as decoration and protection (96). The application is difficult in so far as providing uniformity because of the decidedly nonuniform substrate. Leather coatings also have a requirement for much greater flexibility and extensibility than other coatings. For example, the required resistance to flexural fatigue is very high in the vamp of a shoe where the leather is folded upon itself and straightened with each step for hundreds of thousands of flexes. Also, because of its fibrous network, leather can be stretched greatly multidirectionally and, thus, exert extreme local extensions and stresses in the coatings. This happens particularly in garment leather where the loose fiber weave of goatskins or sheepskins, particularly in the flanks, stretch up to 300% of its original length. The leather finish must undergo such stretching even at subzero temperatures without breaking or checking under the strain.

The ability to meet these demanding requirements for uniformity, flexibility, and extensibility depends to a large extent on primer coatings which are similar in formulation to those of latex house paints (see Paint), but which are made with specially developed emulsion polymers, mostly of the polyacrylate type although butadiene copolymers also are employed. The latex polymers for leather basecoats have to be of exceptionally high molecular weight and exceeding low glass-transition temperature T_g (97).

Unfortunately, latex coatings of the type described offer little protection against abrasion and/or scuffing and higher modulus polymers are required. These are provided in upper coats applied from solvent solutions. The natures of some of the polymer systems have been reviewed (98). Mostly nitrocellulose or vinyl chloride copolymer lacquers are employed. Polyurethanes are used increasingly, but their principal application for leather has been in the specialized production of patent-leather coatings where thermoplastic, followed by moisture-cured, polyurethanes have completely replaced the bodied linseed-oil varnishes that used to be employed (see Urethane polymers).

If the high modulus polymer topcoats are applied directly over the extremely low modulus basecoats, the difference in modulus leads to intercoat failure during flexing.

It is necessary to provide multiple coatings with a gradually increasing modulus in each coat from bottom to top. This prevents a stress build-up within any particular coating. Usually no less than three and, more often, four or five coats are employed. The development of a class of vinylidene chloride-acrylate latex copolymers (99), which are partially crystallizable and, although of low glass-transition temperature, are less thermally sensitive and of somewhat higher modulus than equally low T_g polyacrylates, has been found to aid the transition.

An additional benefit of using multiple coatings is the achievement of special fashion effects; the following example is illustrative:

Semi-aniline shoe-upper leather coating

1. Light-colored pigmented base coat (seasoning machine application): 38.1 μm coating with low T_g polyacrylate.

2. Same color pigmented latex spray coat (spray machine): 25.4 μm coating with slightly higher T_g vinylidene chloride-acrylate copolymer.

Smooth and fuse to the leather at 10.3 MPa (1500 psi) in a heated press at 94°C.

3. Spray with light-colored, highly plasticized nitrocellulose solution coating (ca 17.8 μm) containing organic pigment that is similar in color but livelier in appearance than the pigmented base coats. Level by plating at 104°C, 13.8 MPa (2000 psi).

4. Spray with a slightly less plasticized nitrocellulose coating (ca 7.6 μm) containing a transparent organic dyestuff of darker color than the color formerly employed. Spray at an angle to get uneven dye application for special effect desired. This will give an uneven transparent look with the bright, solid, lively color underneath showing through.

5. Spray with a clear nitrocellulose top (ca 12.7 μm) that is low in plasticizer to obtain abrasion resistance. Use a smooth plate in the press at high temperature (ca 110°C). Use just enough pressure to provide smoothness and slip to the surface. The leather resulting from this process will be lively, deep-toned, and rich in appearance.

To preserve the long-term flexibility achieved in the base coats by high molecular weight emulsion polymers, the polymers used in the upper coats also have been of as high a molecular weight as was practically feasible but with limited solubility. Almost all upper coats for leather have been at 10% or less solids. Hence, 90% of the coatings' weight has entered the environment as volatile organic compounds (VOC). The EPA has recommended limiting VOC of surface coatings to much lower solvent emissions for a series of industries (100) and is expected to do so for leather coatings also. Consequently, emphasis is being placed on potential utilization of water-based upper coats, which include not only the vinylidene chloride-acrylate copolymer latex topcoats (97) but water-based polyurethanes (101-102) and tougher water-based acrylics (103).

These water systems do not provide the liveliness, clarity, gloss, and fashion effects that are obtainable with the current solvent system upper coats. Early reports of radiation-curable, 100% active leather-coating systems may permit avoidance of this difficulty (104-105). Such radiation-curable systems consist of coatings in which the only solvents employed are acrylic or other vinyl monomers. The leather and its wet coating are passed under a beam of electrons or strong ultraviolet light; polymerization occurs in seconds, and the solvents, instead of evaporating, become part of the coating. The coatings have good gloss and clarity, solvent is not emitted to the environment, and energy and space requirements are reputed to be far less than in conventional ovens (see Radiation curing).

A special treatment was introduced into leather finishing during the 1960s which has assumed considerable commercial importance, particularly for corrected grain leathers. This was the development of specially penetrating polymeric precoat systems that migrate rapidly into the thermoplastic or grain layer of the leather to fill this upper layer with reinforcing polymers which reduce scuffing of the leather and improve its handling in the shoe factories. In addition, the break or fine folds in the leather surface are greatly improved in appearance so that the coarser grain surface appearance of shoe-upper leathers made from steer and cowhides could rival or even surpass the appearance of fine calfskin leathers after repeated flexing of both types of leather. Specially developed polymers were of acrylic (106-108), polyurethane (109) and acrylic-urethane copolymer (110) types. Because of greater ease in handling, lower cost, and better break improvement, acrylics have been favored. The modes of action and general requirements for the polymers involved have been described (111). In recent years, the process of making leather/polymer composites in conjunction with the normal wet-processing operations prior to finishing has been receiving considerable attention both in the U.S. Department of Agriculture's Eastern Regional Research Center (62-77) and in the Central Leather Research Institute at Madras, India (79-80). Evidence of grafting monomers onto the leather protein structure to form new chemical entities has been adduced. The degree of grafting has since been questioned (112-113) but whatever the mechanism, the modification of leather is sufficiently great to introduce new sets of properties. One startling example is the development of shearling and garment leathers whose polymer, fatliquor, and dyes are unextractable with dry cleaning solvents so that they have been successfully cleansed in consumer, coin-operated, cleaning machines (114).

Energy Consumption. On the basis of quantity of energy consumed per unit of product produced, the leather-manufacturing industry would be categorized with the aluminum, paper, steel, cement, and petroleum-manufacturing industries as a gross consumer of energy (115). Since the leather manufacturing industry does not produce the quantities that these other industries produce, its total energy consumption is considerably less. Studies made during the petroleum shortage in the early 1970s indicated that the leather-manufacturing industry was highly wasteful in its energy usage. Estimates at that time indicated that only ca 30% of the energy consumed was required on a theoretical basis. With the inefficiencies that exist in energy conversion and usage, it certainly would not be possible to eliminate all of the waste. However, an energy wastage in the amount of 70% of energy input offers considerable opportunity for improvements.

About 40% of the energy used by the tanning industry is consumed in drying the leather, but only about one quarter of this was needed. The remaining three-quarters, or 30%, of the industry usage was wasted by inefficiencies in the drying equipment and as exhaust air. Since that time, improvements have been made in the drying operation, but there are no estimates as to how great these improvements are. Obviously, the potential exists for substantial savings in this operation.

Finishing of the leather consumes another 37% of the total energy consumption. By the use of new technology for applying and curing finishes, substantial savings could be realized. In particular, gravure coating of leather is a practical, energy-efficient method of finish application (116) and switching from thermally-cured finishes to radiation-cured finishes would be extremely beneficial (104).

The beaming and tanning of the hides account for only ca 13% of the total energy

consumption, with the possibility for a proportionately smaller savings of energy. The final 10% of the energy consumption is what has been labeled comfort heat, which is apparently well used, with the potential of extremely small savings.

A 15% reduction in energy consumption could be realized with minimum investment and up to 30% could be achieved after substantial investment in auxiliary equipment. Beyond this point, significant changes in currently used processes would be required. Some of the modifications to current processing technology that are made in order to reduce pollution also reduce energy consumption. Process modifications that result in lower water usage reduce not only the total effluent discharge from the tannery but reduce the energy required to bring the water to process temperatures.

Economic Aspects

Hides of bovine cattle are the primary raw material used in the United States leather-tanning industry. In 1978, 84% of the leather produced in the United States came from bovine hides. The leading animal skin alternative is sheepskin; however, the number of sheep in the U.S. has been declining steadily. Alternative animal skin sources include pigskins, goatskins, horsehides, and deer and elk hides. Pigskins probably will be the best alternative for cattlehides. Current pigskin production for leather manufacture is estimated at ca 3×10^6 skins annually, with four pigskins being equivalent to one cattlehide in area. However, recent technological developments in skinning swine carcasses offer some potential for increased availability (117).

World production of hides and skins in 1977 and 1978 was ca 4.5×10^6 metric tons (118). The United States is the largest leather-producing country and accounts for just over one fourth of the world production. World trade in hides and skins was ca 1.6×10^6 t in 1977 and 1978, and the United States accounted for ca 44% of this trade which amounts to ca 60% of United States production. In the U.S., the bulk of the hides (almost 70%) are produced in the midwest and southwest parts of the country.

The marketing of hides, worldwide, has been undergoing changes. Other principal producers of cattle have limited their supplies of cattlehides to the rest of the world in order to encourage their own tanning industries and to improve their balance of payments. As a result, the United States has become almost the sole source of cattlehides in international trade. Also, the bottom of a cattle population cycle was reached, and the resulting scarcity of hides caused a doubling of hide prices within 4–6 mo. The demand for leather worldwide far exceeded the supply of raw material, and over 60% of the domestically produced hides in the U.S. were exported. As a direct result of these exports, wettings, ie, hides entering processing, decreased from a high of ca 20×10^6 hides in 1976 to ca 15×10^6 hides in 1979. There is considerable pressure to slow or stop exportation of raw hides and, instead, to export partially processed hides. The latter practice is increasing and may provide an important export market commodity. In addition, alternative leathermaking raw materials are being sought; there is considerable potential for pigskins to meet this need. Pigskin leather may become a major lightweight shoe and garment material in the 1980s.

When a hide is removed from the carcass, the first concern is to preserve or cure that hide so that it is protected until it can be transported to a tannery for manufacture into leather. When time and labor were less expensive, this was done by salting the hides in a solid pack. Hides were laid out flat and covered with a minimum of 1 kg salt/kg hide. The salt dissolved in the water in the hide, formed brine, and dehydrated

the hide. Dehydration inhibits autolysis and the growth of bacteria. After the hides had drained for 30 d, they were sorted and bundled for delivery to the various tanners. Today the vast majority of hides are cured in a saturated salt solution in a raceway that can hold several hundred hides. They are continually tumbled in this salt solution, which is held at saturation and, thus, removes water from the hide to prevent microbial growth. A bactericide also is added to assist in preserving the hides. Full salt penetration and dehydration require from 18–24 h. The cured hides generally are fleshed to remove fatty tissue adhering to the underside of the hide and they are sorted, bundled, and tied for shipment. This whole process can be carried out within 2–3 d, and large inventories are no longer necessary.

Hides are sold in a variety of categories, the main types being steerhides and cowhides. They may be native, butt-branded, or Colorados. Native means that there are no brands; a butt-branded animal is branded within 30 cm forward of the tail, and Colorados are branded on the side beyond 30 cm from the tail. Each type is sold in several weight classes. From this variety of selections the tanner chooses the best starting material for the particular leather to be manufactured. One of the unique aspects of this industry is that its raw material is bought by weight, and the product is sold by area. Naturally, the tanner buys the material which optimizes output in area of leather per unit weight of starting raw material. The exception to this is sole leather which is sold by weight.

In 1978, there were an estimated 380 plants involved in tanning and finishing leather in the U.S. (118). These plants belonged to 187 companies and were concentrated in seven states: California, Maine, Massachusetts, New Jersey, New York, Pennsylvania, and Wisconsin, and employed ca 21,500 workers. They sold over half of their leather to the footwear industry with the balance going into leather garments, gloves, handbags, belts, and miscellaneous products.

Health and Safety Factors

In 1973, the U.S. EPA published (119) a set of proposed regulations designed to control effluent quality in the leather manufacturing industry. These standards were rejected by the courts, and a second proposal was issued to the industry in 1979 (120). Whether or not these also are changed by the courts, it is clear that the industry must clean its effluents; however, some of the smaller tanners will not have the capital to invest in the necessary equipment. Clean air and water laws also are having an affect. In 1970, there were 400 tanneries in the U.S.; in 1979, there were only 208.

The effluent streams which must be treated can be separated into two areas of the tanning operation, the beamhouse and the tanyard. The main pollutants found in beamhouse effluent are sulfide and BOD, and the pH is ca 12. It typically contains sulfide and is saturated with $\text{Ca}(\text{OH})_2$. Dissolved sulfide under neutral or acid conditions forms the poisonous gas, hydrogen sulfide. Accidental release of this gas has been responsible for the death of a number of tannery workers over the last few years. Some type of oxidation, eg, catalytic (manganous salts) or chemical (peroxide or permanganate), may be used to convert sulfide to sulfate. The second major component of the beamhouse waste treatment is BOD from the hair dissolved in the unhairing step. Keratin can be removed by acid precipitation or by biological treatment in a conventional activated-sludge treatment plant. A physical-chemical approach, which was developed by the USDA, provides for simultaneous recovery of the sulfide for reuse

in the tannery and most of the protein as a solid cake, which may be used as a feed supplement or disposed of as a solid waste (see Pet and other livestock feeds).

The second, and even more difficult, stream to treat is that from the tanning operation. This effluent contains chromium as well as conventional pollutants, eg, BOD and suspended solids. All wastes containing chromium are considered by EPA to be hazardous. This is a controversial classification of real importance to the tanning industry. Chromium ions in the 3+ valence state have not been demonstrated to be harmful to either plants or animals; there is evidence that chromium is a micronutrient necessary for proper growth. On the other hand, chromium in the 6+ state in certain salt combinations has been shown to be toxic and carcinogenic. The EPA regulations proposed for 1984 set a limit of 3 ppm total chromium for indirect dischargers [effluent goes to publicly owned treatment plant (POTW)] and 0.5 ppm for direct discharges into a river or stream. With current technology, these will be difficult limits to meet. It is expected that recycling of chrome tanning solutions or recovery and reuse by precipitation of the chrome is needed to achieve these limits. Meeting the pretreatment limitations for the conventional pollutants can be achieved with conventional biological treatment. Direct discharges need some type of tertiary treatment, possibly followed by some polishing steps.

Once effluent quality is achieved, however, the tanner faces another problem: solid waste containing chromium is considered hazardous and must be disposed of in a sanitary landfill. This presents an additional expense over disposal in an unsecured landfill and the number of available sites for sanitary landfills is decreasing rapidly. One solution is to find a by-product use for the solid wastes that contain chromium. A second possible route is the incineration of chrome wastes and recovery of chrome for reuse (see also Recycling, metals).

The finishes that conventionally are applied to leather are contained in a variety of solvents that are removed during drying and enter the atmosphere. The concentration and quantity of VOC are being regulated in some states. The solution is either energy-consuming combustion processes to remove the VOC or a change in the finishing technology.

Uses

In 1978 the United States leather manufacturing industry had estimated shipments of 1.5×10^{12} of leather (99), and the principal domestic markets for this leather were in leather footwear ($\$4 \times 10^9$), luggage ($\660×10^6), handbags ($\$570 \times 10^6$), small personal leather goods ($\$410 \times 10^6$), leather apparel ($\280×10^6), and gloves ($\$180 \times 10^6$). These industries, however, lack developing technology and, consequently, have low productivity and they continue to be pushed out of the market by importers of leather and leather goods. In 1978, leather and leather goods imports into the United States were valued at $\$3.2 \times 10^9$ and exports of hides and skins, leather, and leather goods amounted to $\$700 \times 10^6$, resulting in a net deficit in the balance of (leather) trade of $\$2.5 \times 10^9$. It is encouraging to note that United States tanners are turning to overseas markets for their leather with some degree of success. Another interesting trend is the construction by Western European shoe companies of shoe manufacturing facilities in the United States, which could provide additional markets for United States leather.

Hide Uses. Various components of the hides not made into leather constitute by-products, some of which have value. Hide collagen, when it can be separated from the hide in a native state, has use in food products, cosmetics (qv) pet treats, and biomedical products. Hide collagen that has been tanned or treated with biocides and other hide materials has some uses but, in many cases, is a waste product. The greater use that is made of these hide components, the greater the return is to the tanner and the lower the cost of manufacture of the principal product, leather. Compositionally, collagen is low in several essential amino acids and totally lacks tryptophan; hence, it is not a nutritionally complete protein. Its use in foods depends on other, mainly physical, properties which it possesses; the same is true concerning its use in cosmetics and biomedical products. Because collagen is a nonspecific protein, it can be used in cosmetics (eg, in moisturizing creams, lotions, and hair sprays) and biomedical products (eg, burn dressings, implant coverings, and as a hemostat), since it does not cause an allergic response when used on or in the body. Its use as a pet treat depends on the fact that it has a texture that dogs prefer for chewing and can easily be flavored.

The collagen used in these applications is obtained mainly from limed splits. These are provided by tanners who split the hides to the desired thickness for grain leather manufacture following the unhairing and reliming steps rather than after tanning. The split has been thoroughly cleaned of extraneous material, is relatively free of bacterial contamination (pH 12.5), and is stable for a short period of time. For some applications, only uncured hides have been used for production of the limed splits to avoid any possible residual contamination with the biocides commonly used in hide curing. This practice, however, requires that the hides be processed within a relatively short time after removal from the animal. Aside from gelatin manufacture, the largest food use is in sausage casings; however, its use in other food products is being studied. It is expected that the nonleather uses for hide collagen will grow.

By-Products. The weight of finished grain leather generally is from 20–30% of the weight of the hide, depending on the thickness of the leather and the rawhide selection (121–122). The remaining 70% consists of either by-products that can be sold or wastes that must be disposed of. Over the years, as markets have changed, some wastes have become by-products and various by-products have become wastes. The largest by-product by weight is the split. It may account for from 30–50% of the incoming hide. If the hide is split right after the liming operation, the option to use the split for collagen casings is available. If it is split in the blue, it can be sold to a split tanner to be made into split leather. Although this market fluctuates, the split is almost always a salable by-product.

Another 15% of the raw hide appears in the effluent as dissolved and suspended organic matter which consists largely of the protein that was dissolved in the beam-house processes. Some potential exists for obtaining this protein in a form that could be used for animal feed. However, this generally is not done and the protein is considered a waste requiring disposal. One reason that the protein is not recovered is that there is not enough in the effluent of a single tannery to make recovery economically worthwhile. This is a general problem with by-products of the tanning industry.

Twenty percent of the raw hide shows up as solids that contain chromium. In the form of shavings, blue trim, buffing dust, and crust trim, these solids offer potential for some type of leather fiberboard product, although little if any is produced right now, and most tanners must pay to have the chromium by-products hauled away. Once again, the individual tanner frequently does not handle enough raw hide to produce leather fibers economically.

About 5% of the hide coming into the tannery ends up as raw material for a renderer. The value of fleshings is lowered if they are from salted hides. The remaining 7% of the hide is composed of solids not containing chrome, primarily the trim which sometimes can be sold along with the fleshings to the renderer; otherwise, it is considered a solid waste.

Cattle-hair markets have almost disappeared because, with the advent of hair burning or dissolving processes, which rapidly remove the hair from the hide, no hair is left. This once salable by-product has become an effluent problem.

BIBLIOGRAPHY

- "Leather and Tanning" in *ECT* 1st ed., Vol. 6, pp. 289-309, by Fred O'Flaherty, University of Cincinnati;
- "Tanning Materials" (in three parts) in *ECT* 1st ed., Vol. 13, pp. 578-599 by F. L. Hilbert, U.S. Process Corp., and R. L. Stubbings, Lehigh University; "Leather" in *ECT* 2nd ed., Vol. 12, pp. 303-343, by F. O'Flaherty, University of Cincinnati, R. L. Stubbings, Institute of Leather Technology.
1. F. O'Flaherty, W. T. Roddy, and R. M. Lollar, eds., *The Chemistry and Technology of Leather*, Vol. I-IV, Reinhold Publishing Corp., New York, 1956-1965.
2. J. R. Kanagy in ref. 1, Vol. IV, 1965, pp. 369-416.
3. W. T. Roddy, J. Jacobs, and J. Jansing, *J. Am. Leather Chem. Assoc.* **44**, 308 (1949).
4. G. O. Conabere and R. H. Hall in *Progress in Leather Science, 1920-1945*, British Leather Manufacturers' Research Association, London, 1948, pp. 265-279.
5. W. T. Roddy, R. Echerlin, and J. Jensing, *Quartermaster General's Research Reports on Leather Technology*, April 15, 1948.
6. *United States Military Specification MIL-L-3122*.
7. J. A. Wilson, in *International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*, Vol. II, McGraw-Hill Book Co., Inc., New York, 1927, pp. 250-254.
8. M. P. Balfe and F. E. Humphreys in Ref. 4, p. 417.
9. R. A. Vickers, *Leather Manuf.* (Sept. 1950).
10. S. S. Kremen and R. M. Lollar, *J. Am. Leather Chem. Assoc.* **46**, 34 (1951).
11. J. A. Wilson, *Modern Practice in Leather Manufacture*, Reinhold Publishing Corp., New York, 1941, pp. 629-704.
12. S. J. Kennedy, Quartermaster General Research Laboratory, Natick, Massachusetts, personal communication.
13. R. G. Mitton, *J. Soc. Leather Trades Chem.* **31**, 44 (1947).
14. J. A. Wilson and G. O. Lines, *Ind. Eng. Chem.* **17**, 570 (1925).
15. R. S. Edwards, *J. Int. Soc. Leather Trades Chem.* **16**, 439 (1932).
16. J. R. Kanagy and R. A. Vickers, III, *J. Am. Leather Chem. Assoc.* **45**, 211 (1950).
17. J. R. Kanagy and R. A. Vickers, *J. Res. Natl. Bur. Stand.* **44**, 347 (1950).
18. G. N. Ramachandran, ed., *Treatise on Collagen*, Vol. 1, Academic Press, New York, 1967.
19. B. S. Gould, ed., *Treatise on Collagen*, Vol. 2, Academic Press, New York, 1968, Parts A and B.
20. J. H. Highberger in ref. 1, Vol. I, 1956, pp. 65-193.
21. R. M. Koppenhoefer in ref. 1, Vol. I, 1956, pp. 41-64.
22. A. L. Everett and R. J. Carroll, *Leather Manuf.* **82**(8), 29 (1965).
23. W. T. Roddy in ref. 1, Vol. I, 1956, pp. 4-40.
24. M. Dempsey in ref. 4, 1948, pp. 3-27.
25. *Hides, Skins, and Leather Under the Microscope*, British Leather Manufacturers' Research Assoc., Surrey, Eng., 1957.
26. F. Karl and R. M. Schwartzman, *Veterinary and Comparative Dermatology*, J. B. Lippincott Co., Philadelphia, Pa., 1964.
27. T. C. Thorstensen, *Practical Leather Technology*, Robert E. Krieger Publishing Co., Inc., Huntington, New York, 1975.
28. J. J. Tancous, W. T. Roddy, and F. O'Flaherty, *Skin, Hide, and Leather Defects*, Tanners' Council Research Laboratory, Cincinnati, Ohio, 1959.
29. A. L. Everett, N. W. Hooven, Jr., J. Naghski, and R. G. Koeppen, *J. Am. Leather Chem. Assoc.* **70**, 188 (1975).

30. A. L. Everett, R. W. Miller, W. J. Gladney, and M. V. Hannigan, *J. Am. Leather Chem. Assoc.* **72**, 6 (1977).
31. A. L. Everett, I. H. Roberts, and J. Naghski, *J. Am. Leather Chem. Assoc.* **66**, 118 (1971).
32. A. L. Everett and M. V. Hannigan, *J. Am. Leather Chem. Assoc.* **73**, 458 (1978).
33. *Tanners' Council News*, (Feb. 3, 1976).
34. N. P. Slabbert, *Proc. XIV Congr. Int. Union Leather Chem. Technol. Socs.* **I**, 240 (1975).
35. H. M. N. H. Irving, *J. Soc. Leather Technol. Chem.* **58**, 51 (1974).
36. S. G. Shuttleworth in ref. 1, Vol. II, 1958, pp. 281-322.
37. S. G. Shuttleworth, *J. Soc. Leather Trades Chem.* **47**, 143 (1963).
38. I. C. Somerville in ref. 1, Vol. II, 1958, pp. 323-348.
39. N. P. Slabbert, *Proc. XVI Congr. Int. Union Leather Chem. Technol. Socs.* **II**, 88 (1979).
40. A. Zissel in ref. 39, p. 52.
41. C. W. Beebe, W. F. Happich, F. P. Luvisi, and M. V. Hannigan, *J. Am. Leather Chem. Assoc.* **52**, 560 (1957).
42. C. Krawiecki in ref. 39, p. 71.
43. H. R. Procter, *The Principles of Leather Manufacture*, E. & F. N. Spon, Ltd., London, 1922.
44. P. Chambard in ref. 1, Vol. II, 1958, pp. 349-387.
45. J. R. Kanagy, *J. Am. Leather Chem. Assoc.* **33**, 565 (1938).
46. S. T. Tu, *J. Am. Leather Chem. Assoc.* **43**, 181 (1948).
47. J. A. Wilson, *J. Am. Leather Chem. Assoc.* **32**, 113, 494 (1937).
48. U.S. Pats. 2,140,041 (Dec. 13, 1939); 2,140,042 (Dec. 13, 1939); 2,172,233 (Sept. 5, 1940), J. A. Wilson (to Hall Laboratories, Inc.).
49. Ger. Pats. 671,019 (Jan. 30, 1939); 671,712 (Feb. 14, 1939); 672,747 (March 9, 1939), K. Lindner (to Chemische Fabrik J.A. Benckiser G.m.b.H.).
50. K. Lindner, *Collegium* **816**, 146 (1938).
51. R. Lasserre, *Bull. Assoc. Fr. Chim. Ind. Cuir Doc. Sci. Tech. Ind. Cuir.* **18**, 9 (1956).
52. R. S. Meldrum, *J. Soc. Leather Trades Chem.* **37**, 278 (1953).
53. K. H. Gustavson and A. Larsson, *Acta Chem. Scand.* **5**, 1221 (1951).
54. H. G. Turley in ref. 1, Vol. II, 1958, pp. 388-407.
55. Austria Pat. 58,405 (1911), E. Stiasny.
56. H. G. Turley, *J. Am. Leather Chem. Assoc.* **40**, 58 (1945).
57. P. S. Chen in ref. 1, Vol. II, 1958, pp. 408-425.
58. W. C. Prentiss and C. R. Sigafos, *J. Am. Leather Chem. Assoc.* **70**, 481 (1975).
59. W. C. Prentiss and J. J. Hodder, *IV Encontro Nacional dos Quimicos Tecnicos da Industria do Couro*, Rio de Janeiro, 1979.
60. A. Kuntzel in ref. 1, Vol. II, 1958, pp. 426-454.
61. E. H. Farmer, *Trans. Faraday Soc.* **38**, 340, 356 (1942); **42**, 228 (1946).
62. A. H. Korn, S. H. Fearheller, and E. M. Filachione, *J. Am. Leather Chem. Assoc.* **67**, 111 (1972).
63. S. H. Fearheller, M. M. Taylor, and A. H. Korn, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **13**, 359 (1972).
64. S. H. Fearheller, E. H. Harris, Jr., A. H. Korn, M. M. Taylor, and E. M. Filachione, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **13**, 736 (1972).
65. A. H. Korn, M. M. Taylor, and S. H. Fearheller, *J. Am. Leather Chem. Assoc.* **68**, 224 (1973).
66. E. H. Harris, M. M. Taylor, and S. H. Fearheller, *J. Am. Leather Chem. Assoc.* **69**, 182 (1974).
67. U.S. Pat. 3,843,320 (Oct. 22, 1974), S. H. Fearheller, A. H. Korn, E. H. Harris, Jr., E. M. Filachione, and M. M. Taylor (to U.S.D.A.).
68. S. H. Fearheller, H. A. Gruber, M. M. Taylor, and E. H. Harris, Jr., *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **17**, 814 (1976).
69. E. H. Harris, Jr. and S. H. Fearheller, *Polym. Eng. Sci.* **17**, 287 (1977); *AIChE Sym. Ser.* **74**, 131 (1977).
70. A. H. Korn, E. H. Harris, and S. H. Fearheller, *J. Am. Leather Chem. Assoc.* **72**, 196, abstr. of presentation (1977).
71. H. A. Gruber, E. H. Harris, Jr., and S. H. Fearheller, *J. Appl. Polym. Sci.* **21**, 3465 (1977).
72. M. M. Taylor, E. H. Harris, and S. H. Fearheller, *J. Am. Leather Chem. Assoc.* **72**, 294 (1977).
73. M. M. Taylor, E. H. Harris, and S. H. Fearheller, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **19**, 618 (1978).
74. H. A. Gruber, E. H. Harris, and S. H. Fearheller, *J. Am. Leather Chem. Soc.* **73**, 410 (1978).

75. H. A. Gruber, M. M. Taylor, E. H. Harris, and S. H. Fairheller, *J. Am. Leather Chem. Assoc.* **73**, 530 (1978).
76. M. M. Taylor, M. V. Hannigan, and E. H. Harris, *J. Am. Leather Chem. Assoc.* **74**, 167, abstr. of presentation (1979).
77. E. H. Harris, H. A. Gruber, and M. M. Taylor, *J. Am. Leather Chem. Assoc.* **75**, 6 (1980).
78. J. Kudaba, E. Ciziunaite, and D. Jonutiene, *Liet. TSR Aukst. Mokyklu Mokslo Darb. Chem. Chem. Technol.* **10**, 147 (1969); *Chem. Abstr.* **73**, 4982b (1970).
79. K. P. Rao, K. T. Joseph, and Y. Nayudama, *J. Polym. Sci. A-1* **9**, 3199 (1971).
80. K. P. Rao, K. T. Joseph, and Y. Nayudama, *J. Appl. Polym. Sci.* **16**, 975 (1972).
81. K. Studniarski and A. Alabrudzinska, *Leder* **30**, 49 (1979).
82. W. O. Lundberg, ed., *Autoxidation and Antioxidants*, Vol. I, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1961.
83. *Austauschfettstoffe für Leder*, booklet by I. G. Farbenindustrie, Frankfurt am Main, FRG.
84. G. W. Schultz and A. Schubert, *An Investigation of the Leather Industry*, Technical Report by Office of Quartermaster General, APO 757, 1945.
85. C. F. Payan, *Some Aspects of the German Leather Industry*, Technical Report by British Intelligence Objectives Subcommittee BIOS Final Report No. 150, Item 22, Sept.-Oct. 1945.
86. J. B. Brown, M. F. White, W. T. Roddy, and F. O'Flaherty, *J. Am. Leather Chem. Assoc.* **42**, 625 (1947).
87. E. F. Mellon in ref. 1, Vol. II, 1958, pp. 66-97.
88. J. W. Harlan and S. H. Fairheller in M. Friedman, ed., *Protein Crosslinking Nutrition and Medical Consequences*, Vol. 86A, Plenum Publishing Corp., New York, 1977, pp. 425-440.
89. J. S. Kirk in ref. 1, Vol. III, 1962, pp. 1-15.
90. G. Otto in ref. 1, Vol. III, 1962, pp. 16-60.
91. C. E. Retzsch in ref. 1, Vol. III, 1962, pp. 61-72.
92. M. H. Battles in ref. 1, Vol. III, 1962, pp. 73-107.
93. C. F. Dudley in ref. 1, Vol. III, 1962, pp. 108-126.
94. L. Buck in ref. 1, Vol. III, 1962, pp. 127-183.
95. M. Dempsey in ref. 4, pp. 319-414.
96. P. R. Buechler in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Vol. 13, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1970, pp. 486-505.
97. P. R. Buechler, *J. Am. Leather Chem. Assoc.* **72**, 79 (1977).
98. R. Shaw in ref. 1, Vol. IV, 1965, pp. 194-222.
99. U.S. Pat. 3,048,496 (Aug. 7, 1962), P. R. Buechler and B. B. Kine (to Rohm and Haas Co.).
100. *Control of Volatile Emissions from Existing Stationary Sources*, U.S. Environmental Protection Agency, Vols. I-VIII, 1976-1978.
101. V. E. Müller, *Angew. Makromol. Chem.* **14**(203), 75 (1970).
102. G. J. Katz, *Leather Manuf.* **96**(7), 34 (1979).
103. C. E. Cluthe, F. A. Desiderio, and W. C. Prentiss, *J. Am. Leather Chem. Assoc.* **73**, 22 (1978).
104. P. R. Buechler, *J. Am. Leather Chem. Assoc.* **73**, 56 (1978).
105. M. A. Knight and A. G. Marriott, *J. Soc. Leather Technol. Chem.* **62**, 14 (1978).
106. U.S. Pat. 3,103,447 (Sept. 10, 1963), J. A. Lowell, H. L. Hatton, F. J. Glavis, and P. R. Buechler (to Rohm and Haas Co.).
107. U.S. Pat. 3,231,420 (Jan. 25, 1966), J. A. Lowell, E. H. Kroeker, and P. R. Buechler (to Rohm and Haas Co.).
108. Belg. Pat. 637,052, I. V. Mattei (to Rohm and Haas Co.).
109. U.S. Pat. 3,066,997 (Dec. 4, 1962), M. B. Neher and V. G. Vely (to Titekote Corp.).
110. U.S. Pat. 3,441,365 (Apr. 29, 1969), J. A. Lowell and P. R. Buechler (to Rohm and Haas Co.).
111. P. R. Buechler, *Leather Manuf.* **78**(2), 19 (1961).
112. E. F. Jordan, Jr., B. Artymyshyn, A. L. Everett, M. V. Hannigan, and S. H. Fairheller, *J. Appl. Polym. Sci.*, in press.
113. E. F. Jordan, Jr. and S. H. Fairheller, *J. Appl. Polym. Sci.*, in press.
114. S. J. Viola and S. H. Fairheller, *J. Am. Leather Chem. Assoc.* **70**, 227, abstr. of presentation (1975).
115. M. S. Maire and P. A. Sundgren, *Weekly Bull. Leather Shoe News*, Boston, Mass., May 25, 1974.
116. W. C. Prentiss and C. E. Cluthe, *J. Am. Leather Chem. Assoc.* **73**, 471 (1978).
117. S. H. Fairheller, D. G. Bailey, and M. S. Maire, *Leather Manuf.* **97**(2), 10 (1980).
118. *U.S. Industrial Outlook—1979*, U.S. Dept. Commerce, 1979, Chapt. 36, pp. 383-402.

- 119. U.S. Environmental Protection Agency, *Fed. Regist.* 39, 12958 (Apr. 9, 1974).
- 120. U.S. Environmental Protection Agency, *Fed. Regist.* 44, 38747 (July 2, 1979).
- 121. R. Donovan, *Leather Manuf.* 95(7), 16 (1978).
- 122. M. S. Maire, *Leather Manuf.* 93(9), 12 (1976).

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